SOLVENT REDUCED PROCESS FOR FLUORINE-FREE THICK ELECTRODES IN STATIONARY SODIUM-ION BATTERIES

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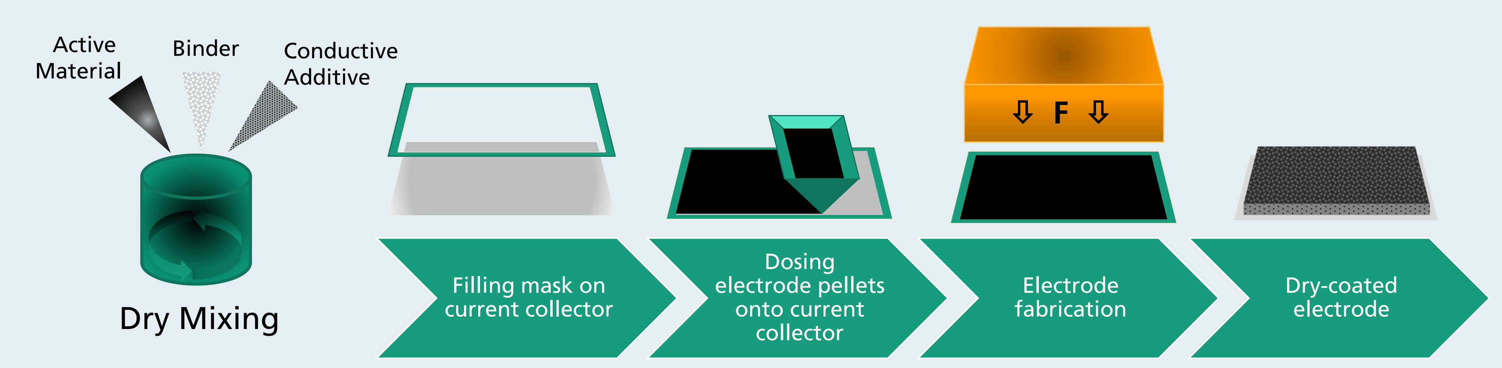
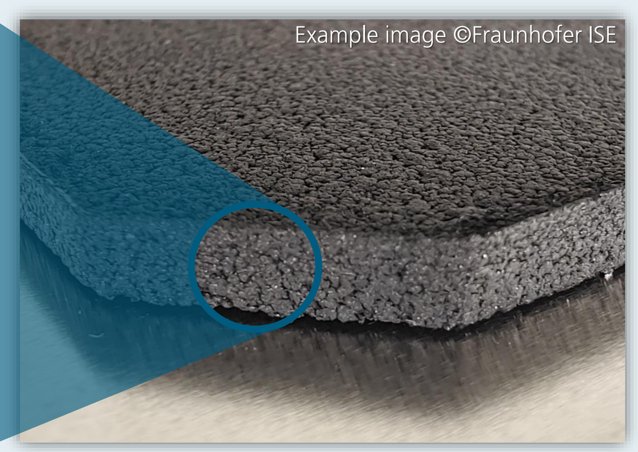
Motivation

Sodium-ion batteries (SIBs) have recently attracted rising attention due to the use of highly available and globally evenly distributed **raw materials**, potential low **cost**, and convincing **performance**. Dry electrode processing for SIBs can enable higher specific energies and reduce costs, whilst showing potential to use fluorine-free binders without the need for *N*-methyl-2-pyrrolidone (**NMP**). Herein, we show promising results for this approach, using a **fluorine-free binder** with ***P2*-$Na_{2/3}Fe_{1/2}Mn_{1/2}O_2$ (NFMO)** as cathode active material and **bio-based Hard Carbons** (HC) in **SIB full-cells** with areal capacities **>4 mAh·cm⁻²**.

Morphology Tuned Thick Electrode Dry Processing



- Ultra-thick electrodes (~0.2 – 5 mm)
- Tunable porous structure
- Tunable pore & solid fraction sizes
- Tailored diffusion for ultra-high loadings
- Increased specific energy



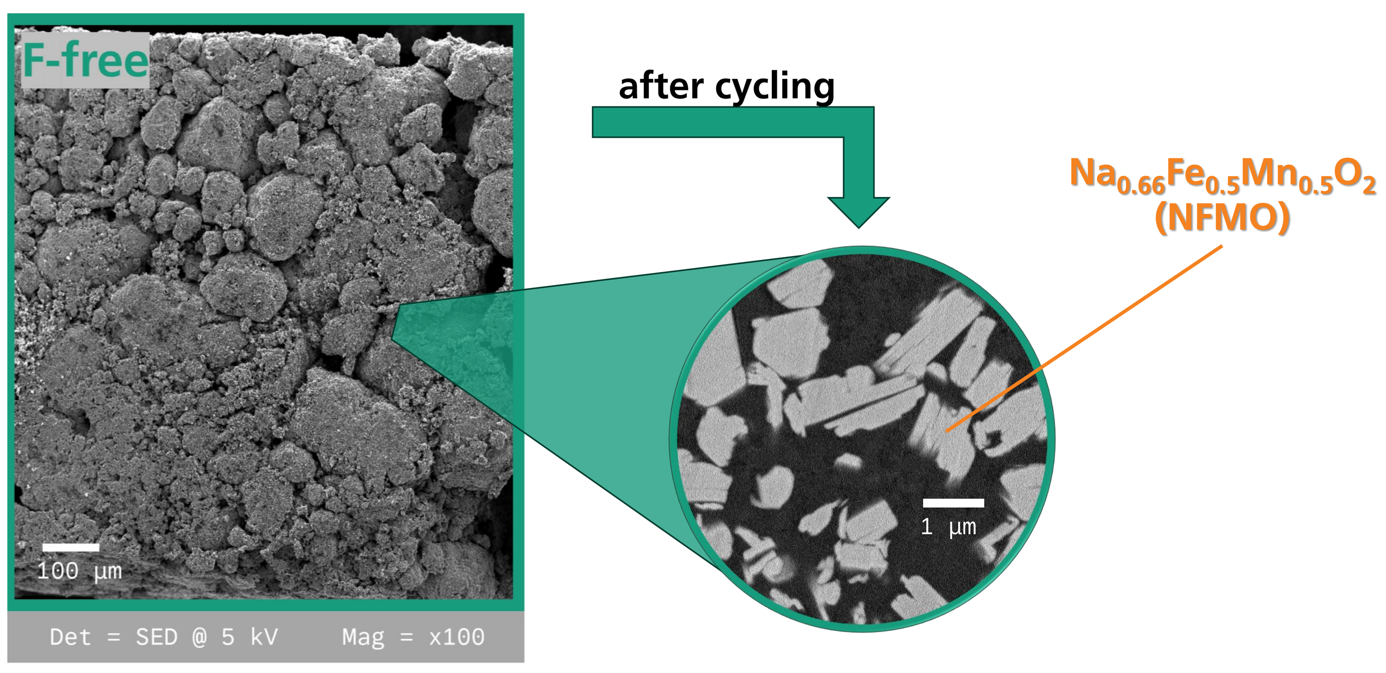
Properties of Dry-Coating Process

Pros

+ Possibility of thick electrodes with high areal capacity & specific energy
+ Solvent-free processing reduces production costs
+ No toxic solvents & no expensive NMP
+ Flexible material composition for flexible cell chemistries
+ Many possible binders

Challenges

- Electronic/ionic conductivity & C-rate capability
- Higher binder & conductive additive content



Experimental – Electrode Preparation

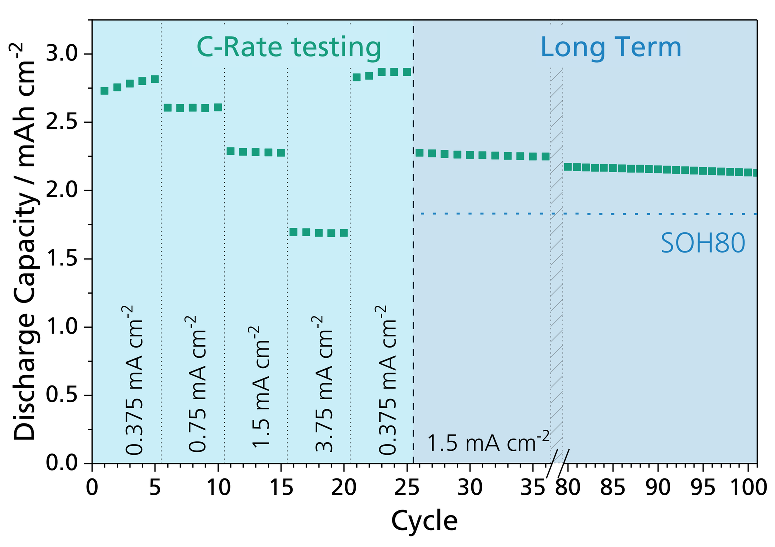
- 80% *P2*-$Na_{2/3}Fe_{1/2}Mn_{1/2}O_2$ (MSE Supplies) & Cellulose-derived Hard Carbon (Fraunhofer ISE)
- Dry-mixed (12% Carbon Black, 8% fluorine-free binder) and structured
- Pressed on Al current collectors
- 18 mm electrodes (<1 mm thickness)

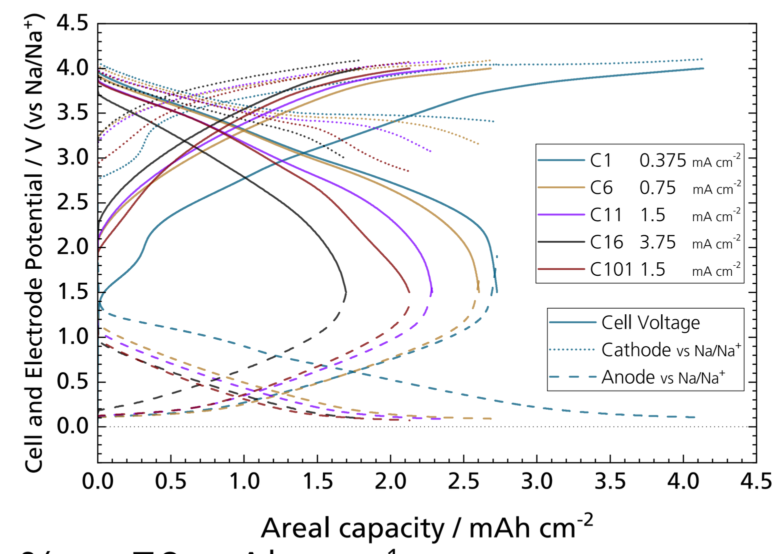
Experimental – Electrochemical Characterization

- Hot-pressed electrodes in EL-CELL® PAT-Cells with 30 µm Delfort IonPort® SC-3042 Cellulose separator, 1 M $NaPF_6$ in EC:DMC (3:7) + 4 % Additives (450 µl) as electrolyte
- Galvanostatic cycling in full-cells (vs. HC) **1.5 – 4.0 V** or **1.5 – 4.25 V**

Results – P2-$Na_{2/3}Fe_{1/2}Mn_{1/2}O_2$ ‖ Hard Carbon Full Cells

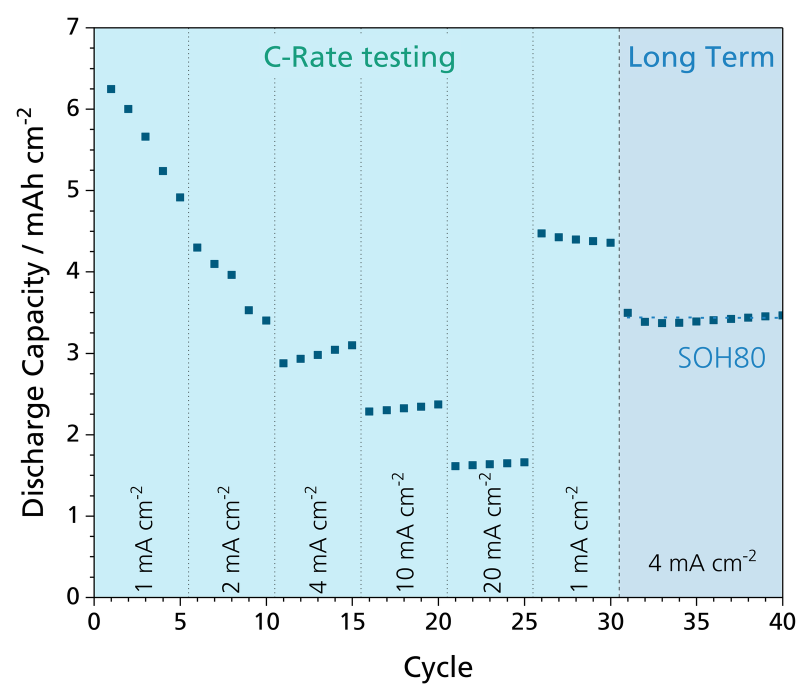
Operating Window 1.5 – 4.0V: Non-plating behavior

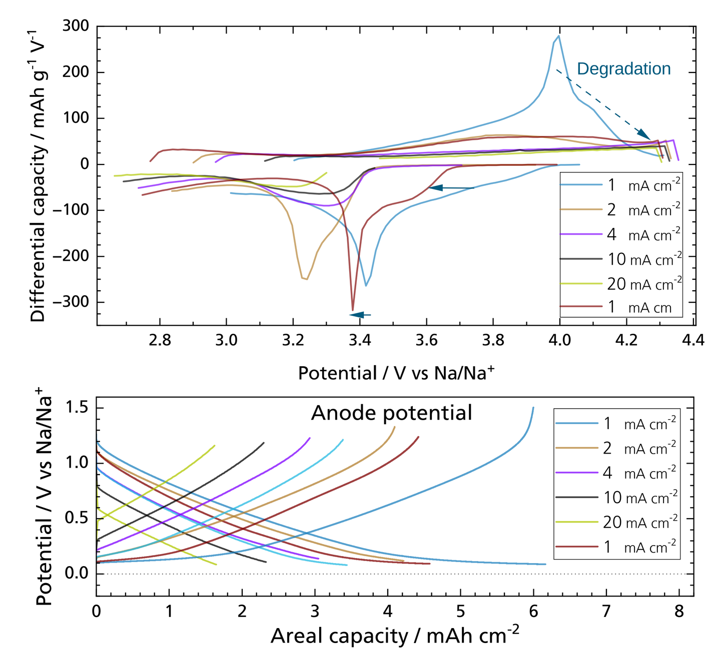




- Relatively high initial losses: iCE = 66 % or 70 mAh g_{HC}^{-1}
- No Na-Metal plating at up to 3.75 mA cm⁻²
- Stable capacities, limited C-Rate capability
- Relatively high overpotentials in cathode for higher currents

Operating Window 1.5 – 4.25V: P2-NFMO Degradation and Anode Potential





- No Na-Metal plating at currents of up to 20 mA cm⁻²
- NFMO: P2-OP4 phase transition >4 V
  - Siginificant loss of capacity
  - Increased hysteresis and slower kinetics

Conclusion & Outlook

✓ Successful application of fluorine-free binder for dry processed cathodes for SIBs enabling capacities >4 mAh cm⁻²
✓ Effective suppression of Na-Metal plating at high areal currents of 20 mA g⁻¹
⌛ Degradation of NFMO >4 V due to phase transition
⌛ Insufficient initial Coulombic Efficiencies

- Optimization of electrode composition (binder & conductive additive)
- Active material optimization
- Electrolyte evaluation

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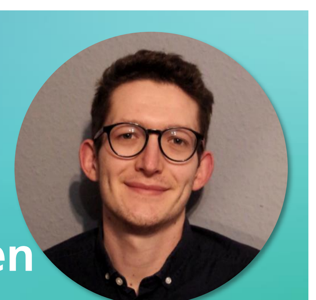

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